PATENT SPECIFICATION

(11) 1 460 480

1 460 480

(21) Application No. 49638/74 (22) Filed 15 Nov. 1974
(31) Convention Application Nos. 422 630 (32) Filed 7 Dec. 1973
422 631 7 Dec. 1973
495 968 9 Aug. 1974 in
(33) United States of America (US)
(44) Complete Specification published 6 Jan. 1977
(51) INT. CL.[2] C10G 23/16 23/02
(52) Index at acceptance
C5E 21H5

(19)

(54) DESULFURIZATION PROCESS

(71) We, TEXACO DEVELOPMENT CORPORATION, a Corporation organized and existing under the laws of the State of Delaware, United States of America of 135 East 42nd Street, New York, New York 10017, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:

This invention relates to the desulfurization of certain petroleum fractions. More particularly, it is concerned with the catalytic hydrodesulfurization of heavy petroleum distillate oils under conditions whereby the throughput and desulfurization of a unit may be increased and the hydrogen consumption in the desulfurization procedure may be reduced with prolonged catalyst life.

The catalytic desulfurization of petroleum hydrocrabons has been well known in the refining industry for many years. It has been discussed quite thoroughly in "Petroleum Processing" November 1956, pages 116-138. The literature discloses reaction conditions, using a fixed bed particulate of catalyst, in the broad ranges of temperatures of from 400-900°F., pressures of from 50-5000 psig, hydrogen rates of from 200-20,000 standard cubic feet per barrel (scfb) and space velocities of 0.1-20 volumes of oil per volume of catalyst per hour (v/v/hr.)

Experience has shown that in the commercial desulfurization of heavy oils such as vacuum gas oils and heavier stocks, that is, oils having an initial boiling point of 500°F. or higher, using fixed beds and conventional desulfurization catalysts, the start-of-run temperature using fresh or freshly regenerated catalyst is preferably between 625 and 650°F. and the end-of-run temperature about 750°F., a gradual increase in temperature being made to compensate for loss of activity of the catalyst throughout the onstream period. Pressures range generally between 500 and 1000 psig with hydrogen rates of 500-2000 scfb. Ordinarily in conventional commercial units the space velocity is controlled to obtain the desired amount of desulfurization with 85-90% desulfurization being considered as the most practical from an efficiency standpoint. For the most part, conventional commercial heavy oil desulfurization units are designed to operate at a space velocity of about 1.

It has been generally accepted in the industry that hydrogen consumption is a function of the amount of desulfurization and that as the percentage desulfurization increases so does the amount of hydrogen consumed. It is also a general belief in the industry that, other things being equal, a decrease in space velocity is required to obtain an increase in desulfurization. It has also been generally accepted that high temperatures result in shortened catalyst life, due to loss of activity on the part of the catalyst through deposition of carbon and, in the case of residue-containing charge stocks, metal-containing compounds on the surface of the catalyst particles.

For ecological reasons, it has become necessary to refine more and more petroleum fractions to reduce the sulfur content thereof, thus making desulfurization costs enormous, not only in the amount of equipment that must be built but also in the costs of processing the various petroleum fractions, such as the energy consumed in heating and pressurizing the petroleum fraction and in the cost of hydrogen consumed. It has been ascertained that process improvements leading to a reduction in hydrogen consumption of 100 scfb, or an increase in desulurization from 90 to 95% or a reduction in pour point of 40°F. would result in a great economic improvement over current operations. It would also be a dis-

tinct improvement in the efficiency of a hydrodesulfurization unit if the catalyst deactivation rate could be reduced, thereby prolonging the onstream periods and reducing the overall down-time for catalyst regeneration.

According to our invention, the efficiency of a desulfurization unit is improved by contacting a sulfur-containing heavy petroleum distillate oil having an initial boiling point of at least 500°F. with added hydrogen at a temperature of from 750 to 850°F., (preferably at a pressure of at least 500 psig, most preferably at a pressure of from 500 to 3000 psig) and a space velocity of from 3 to 10, preferably from 4 to 8, v/v/hr. in the presence of a fixed bed of a particulate hydrogenation catalyst comprising a Group VI A metal and an iron group metal, or compounds thereof, supported on a refractory inorganic oxide, and preferably containing from 0.1 to 5% by weight of a Group VII metal, such as manganese or rhenium, based on the catalyst composite.

Feeds which may be used in the process of our invention are heavy petroleum oil distillate fractions having an initial boiling point of at least 500°F. and preferably at least 625°F. Examples of feeds are gas oils such as vacuum gas oils, heavy coker distillates, coal tar distillates and gas oils obtained from shale, tar sand and the like. Generally, they contain from 0.5 to 5.0 weight % sulfur.

The hydrogen used in our process may be obtained from any suitable source, such as reformer by-product hydrogen, electrolytic hydrogen, or hydrogen produced by the partial oxidation or carbonaceous or hydrocarbonaceous materials followed by shift conversion and CO_3 removal. The hydrogen should have a purity of at least 50% and preferably at least 65% by volume.

The catalyst used in the process of our invention comprises an iron group metal, or compound thereof, composited with a group VI A metal, or compound thereof, on a refractory inorganic oxide support. Suitable iron group metals are particularly nickel and cobalt, used in conjunction with tungsten or molybdenum as Group VI A metals. Preferably, the metals are in the form of the oxide or sulfide. Advantageously the iron group metal is present in an amount between 1.0 and 10% by weight, and the Group VI A metal is present in an amount between 5 and 30% by weight, based on the catalyst composite. Examples of refractory inorganic oxides useful as supports are alumina, magnesia, zirconia and the like or mixtures thereof. In a preferred embodiment the support is composed for the most part of alumina stabilized with a minor amount, e.g. up to 5 wt. % silica.

In accordance with one embodiment of the invention, the deactivation rate of the catalyst is reduced by incorporating a small amount e.g., 0.5-5.0%, preferably from 0.2-2.0% of a Group VII metal e.g. rhenium or manganese, based on the weight of the catalyst composite. These metals or their compounds are particularly effective in reducing the deactivation rate when the catalyst is used at high temperatures such 800-850°F. and high space velocities such as 4-8 v/v/hr.

In accordance with a further embodiment the deactivation rate of the catalyst can also be reduced by adding a small amount, e.g., 0.1-5.0%, preferably from 0.2-2.0% of a noble metal based on the weight of the catalyst composite. Rhodium is particularly effective in reducing the deactivation rate when the catalyst is used at conditions well above the usual commercial conditions, e.g. high temperatures such as 800-850°F. and high space velocities such as 4-8 v/v/hr.

By following the procedure of our invention, when the desulfurization catalyst contains a small amount of noble metal, not only is there a considerable reduction in hydrogen consumption over conventional procedures but in addition, the catalyst life is prolonged.

The catalyst may be prepared by conventional means such as those disclosed in U.S. Patent 2,437,533. The catalyst may be prepared by forming the support which, as mentioned above, is, for example, alumina containing a small amount of silica. The support may then be impregnated with the desired metals by use of a solution of a water-soluble compound of the metal. For example, water solutions of ammonium molybdate, cobalt nitrate, nickel nitrate, ammonium metatungstate, rhodium chloride, manganous nitrate or perrhenic acid may be used for the impregnation. After the impregnation of the catalytic materials on the support, the composite is heated to dry and then calcined for several hours in air at high temperature e.g., 900-1000°F. thereby converting the metals to the oxide.

The catalyst is used as a fixed bed of particles which may be spheroids or cylindroids, the latter being preferred. The oil flow may be either upward or downward with concurrent hydrogen flow, or the flow of oil may be downward counter to upwardly flowing hydrogen. In a preferred embodiment, the hydrogen and the oil both pass downwardly through the fixed bed of catalyst particles.

In commercial installations, it is customary to separate the hydrogen from the desulfurization zone effluent and recycle the separated hydrogen to the desulfurization zone. To prevent the buildup of impurities, such as low molecular weight gaseous hydrocarbons, hydrogen sulfide and ammonia, a portion of the recycled hydrogen may be

bled from the system and replaced with fresh hydrogen. Hydrogen may also be added to the recycle stream to replace that consumed in the desulfurization process. The ammonia and hydrogen sulfide may also be removed from the hydrogen by scrubbing with a methanolamine-water solution.

The following examples are submitted for illustrative purposes only and it should not be construed that the invention is limited thereto.

EXAMPLE I

A West Texas-New Mexico sour vacuum gas oil having a sulfur concentration of 1.85 wt. % (x-ray) is passed in upward flow through a fixed bed of cylindrical pellets of a catalyst comprising approximately 3 wt. % cobalt, 12 wt. % molybdenum, 83.0 wt. % alumina, 2-4 wt. % silica and having a surface area of 290 m^2/g, a pore volume to 0.63 cc/g and an average pore diameter of 82.5A. Desulfurization is effected by passing hydrogen upwardly through the catalyst bed with the feed at a rate of 1500 scfb recycle hydrogen and 500 scfb fresh hydrogen at a pressure of 800 psig. The space velocities and temperature and other data appear below. Run 1 represents a typical commercial operation.

TABLE 1

Run No.	1	2	3	4	5
Temperature °F.	670	670	750	800	850
Space velocity v/v/hr.	1	4	4	4	4
Wt. % sulfur in product (x-ray)	0.22	0.63	0.18	0.06	0.05
% Desulfurization	88	66	90	97	97
Hydrogen consumption, scfb	450	213	350	310	340

It can be seen from the above data that not only can greater desulfurization be effected at a higher temperature and a higher space velocity than are used in conventional hydrogen desulfurization, but it was also found that quite unexpectedly between 750 and 850°F. hydrogen consumption was lower than at other temperatures. This is not insignificant as a reduction in hydrogen consumption of 130 scfb during conventional operation means a saving of more than 1,000,000 cubic feet of hydrogen per day in a 10,000 barrel per day desulfurization unit, which by today's standards is of modest size. Many commercial desulfurization units have a capacity in excess of 20,000 barrels per day. In addition by making changes in the size of pumps, compressors, heaters and other auxiliary equipment the capacity of a conventional unit can be quadrupled. Either of these features represents a tremendous saving in the cost of desulfurizing a petroleum fraction at a time when the petroleum industry is being called on to desulfurize more and more petroleum fractions.

The results of Runs 1, 2, 3 and 4 show the effectiveness of the combination of high space velocity and high temperature. Run 1 shows good desulfurization but high hydrogen consumption. Run 2 shows low hydrogen consumption but a product containing more than 0.5 wt. % sulfur. Runs 3 and 4 with temperatures of 750 and 800°F. and space velocities of 4 show desulfurization to a level below 0.2 wt. %.

EXAMPLE II

This example is a substantial repeat of Example I using the same charge stock and reactor, the significant difference being in the use of a space velocity of 8. Reaction conditions and other data are tabulated below:

TABLE 2

Pressure, psig	800
Temperature, °F.	800
Hydrogen rate, SCFB	2000
Product Sulfur, wt. % (x-ray)	0.18
% desulfurization	90.3
Hydrogen consumption, SCFB	260

The above run shows that a 90% reduction in sulphur can be obtained with a hydrogen consumption of only 260 SCFB. This is substantially the same amount of desulfurization obtained by conventional processing at a space velocity of 1 and a temperature of 670F. However, here the hydrogen consumption is approximately 55% that of conventional processing and the throughput is 8 times as great.

It is also important that the pressure be at least 500 psig. Experimental data has shown that the rate of deactivation of the catalyst at a pressure below 500 psig is approximately ten times as great as the catalyst deactivation rate at a pressure of 800 psig when the reaction conditions encompass the high temperature and high space velocities of our invention.

EXAMPLE III

In this example, the same catalyst and charge stock used in the previous examples are used with the same reactor. Reaction conditions and other data are tabulated below.

TABLE 3

Run. No.	7	8
Pressure, psig	400	800
Temperature, °F	800	800
Space velocity, v/v/hr.	4	4
Recyle hydrogen, SCFB	1500	1500
Fresh hydrogen, SCFB	400	500

Product sulfur, wt. %	0.22	0.06
% desulfurization	88.1	96.7
Hydrogen consumption, SCFB	220	310
Loss in desulfurization activity of catalyst, (% activity per barrel per pound of catalyst)	4.7	0.4

These data show 88% desulfurization with a hydrogen consumption of only 220 scfb. However, at 400 psig the catalyst deactivation rate is considerably greater than at 800 psig.

EXAMPLE IV

This example is similar to Example II, but differs in that the charge is an Arabian vacuum gas oil having an API Gravity of 23.6° and a sulfur content (x-ray) of 2.2% and the catalyst contains 2.4 wt. % nickel and 7.8 wt. % molybdenum as the oxides supported on a silica-stabilized alumina (2.5 wt. % silica based by weight on the catalyst composite). Reaction conditions and other data are tabulated below:

TABLE 4

Run	A	B
Pressure, psig	800	800
Temperature, °F.	825	800
Space velocity, v/v/hr	4	8
Hydrogen rate, scfb	2000	2000
Product sulfur, wt. %	0.18	0.28
% Desulfurization	91.8	87.2
Hydrogen consumption, scfb	315	290

These data show that a nickel-molybdenum catalyst is substantially equivalent to a cobalt-molybdenum catalyst.

EXAMPLE V

This example shows that the presence of rhenium in the catalyst reduces the deactivation rate of the catalyst. The composition of catalyst A is 3 wt. % cobalt, 12 wt. % molybdenum, 3 wt. % silica and the balance alumina. The cobalt and molybdenum are present as the oxides. The catalyst has a surface area of 290 m^2/g, a pore volume of 0.63 cc/g and an average pore diameter of 82.5Å. Catalyst B is the same as catalyst A except that it additionally contains 0.5 wt. % rhenium. The charge stock is a West Texas-New Mexico vacuum gas oil having an API Gravity of 22° and a sulfur content of 1.85 wt. %. In each run the charge is passed concurrently with hydrogen through a fixed bed of catalyst at the constant conditions of 800°F. 400 psig. 4 v/v/hr with 1500 SCFB recycle hydrogen and 500 SCFB fresh hydrogen. The onstream period is reported in terms of barrels of feed per pound of catalyst.

TABLE 5

	% Desulfurization	
Charge	A	B
0.27	88.6	90.2
0.34	89.1	90.2
0.41	88.1	89.7
0.48	87.5	89.1
0.54	87.0	89.1
0.61	84.8	88.6
0.68	84.3	88.6
0.75	84.8	88.6
0.82	85.9	88.6
0.89	84.8	87.5
0.96	84.8	87.0
1.02	83.7	87.5
1.09	83.2	87.5
1.16	83.7	87.0
1.23	83.7	87.5
1.30	83.7	87.0
1.37	83.2	86.8
1.43	82.7	86.4
1.50	82.7	87.0

These data show that there is little difference in the initial desulfurization activity of the catalysts, but that the rhenium-containing catalyst loses its activity at a much slower rate.

EXAMPLE VI

Example V is repeated with catalyst C containing 3 wt. % nickel, 13.6 wt. % molybdenum and the balance alumina. Catalyst D is similar to catalyst C but in addition contains 1.0 wt. % rhenium. The reaction conditions are the same as those of Example V.

TABLE 6

	% Desulfurization	
Charge	C	D
0.20	89.1	91.3
0.28	88.7	90.8
0.35	88.5	90.8
0.42	88.1	89.6
0.49	88.3	90.3
0.56	86.9	90.0
0.63	85.7	89.5
0.70	84.5	89.5
0.77	84.8	89.3
0.84	85.2	89.3
0.91	84.6	89.2
0.98	83.7	89.0
1.05	83.2	89.2
1.12	83.5	88.9
1.19	83.5	88.9
1.26	83.6	88.4
1.33	83.1	88.6
1.40	82.7	88.5
1.47	82.5	88.5
1.54	82.6	88.4

These data show that the addition of rhenium to a nickel-molybdenum on alu-

mina has substantially the same effect as its addition to a cobalt-molybdenum on silica-stabilized alumina.

They also show that the presence of rhenium is effective in slowing the deactivation rate of the catalyst especially at a pressure below 500 psig under which conditions catalysts used for the desulfurization of heavy residue-containing petroleum oils, that is, those having a Conradson Carbon Residue of at least 1.0 wt. % are particularly susceptible to rapid deactivation.

EXAMPLE VII

This is a substantial duplicate of Example VI, except that the Catalyst E contains 1 wt. % manganese and the reaction conditions are 800°F., 350 psig, 6 v/v/hr. with a hydrogen circulation rate of 1500 SCFB recycle hydrogen and 500 SCFB fresh hydrogen.

TABLE 7

	% Desulfurization	
Charge	C	E
0.27	89.7	90.7
0.34	89.1	89.8
0.41	88.7	89.2
0.48	88.4	89.4
0.54	88.2	89.0
0.61	87.4	89.1
0.68	87.0	89.0
0.75	86.5	88.9
0.82	85.2	88.5
0.89	84.4	88.6
0.96	83.6	88.4
1.02	83.0	88.2
1.09	82.3	88.3
1.16	82.7	88.1
1.23	82.0	87.9
1.50	80.4	86.6

These runs show that at a pressure of 350 psig, the deactivation rate of Catalyst C is higher than in Example VI and also that the deactivation rate of Catalyst E is less than that of Catalyst C.

EXAMPLE VIII

This example is similar to Example V with respect to charge stock and reaction conditions, the difference being that catalyst F contains 2 wt. % rhenium. As in the other example, the time on-stream is reported in terms of barrels of feed per pound of catalyst.

TABLE 8

Charge	% Desulfurization	Charge	% Desulfurization
0.27	90.3	0.82	88.8
0.34	90.3	0.89	88.9
0.41	90.1	0.96	88.5
0.48	89.8	1.02	88.0
0.54	89.4	1.09	88.1
0.61	89.0	1.16	87.9
0.68	89.1	1.30	87.6
0.75	88.7	1.50	87.6

A comparison of this example with catalyst A of Example V shows the effectiveness of the addition of 2 wt. % rhenium to the catalyst in reducing the deactivation rate of the catalyst at high temperature and low pressure specifically a temperature of 800°F. and a pressure of 400 psig.

EXAMPLE IX

In this example the catalyst is prepared from catalyst A used in Example V. 180 grams of the catalyst is impregnated with 1.35 grams of rhodium trichloride dissolved in 125 cc. of distilled water. After standing at room temperature with occasional mixing for one hour, the impregnated catalyst is dried at 250°F. for 64 hours. The impregnated catalyst and a sample of catalyst, as purchased, are calcined at 900°F. for 2 hours in a flow of air. The catalysts are then evaluated by desulfurizing a West Texas-New Mexico vacuum gas oil having an API gravity of 22° and a sulfur content of 1.85% by passing the charge in each of Runs G and H with hydrogen through a bed of catalyst at a temperature of 800°F., a pressure of 400 psig and a space velocity of 4 v/v/hr. Hydrogen is introduced with the charge at a rate of 1500 scfb, recycle hydrogen and 500 scfb. fresh hydrogen. The results are tabulated below, the length of the on-stream period being reported in terms of barrels of charge per lb. of catalyst, catalyst G being the catalyst as purchased and calcined (and comprising, as indicated in Example V, 3 wt. % of cobalt, 12 wt. % of molybdenum, and 3 wt. % of silica, the balance being alumina), and H the catalyst containing 0.3 wt. % of rhodium.

TABLE 9

Throughput (bbl./lb.)	*G*	*H*
0.20	91.3	91.8
0.27	90.2	91.3
0.34	89.1	90.2
0.41	88.1	89.7
0.47	87.0	89.1
0.54	87.5	89.1
0.61	86.4	89.1
0.68	85.9	87.5
0.75	85.4	88.1
0.82	84.8	88.1
0.89	85.4	87.5
0.95	84.8	87.5
1.02	84.3	88.1
1.09	84.3	88.1
1.16	84.3	87.0
1.23	84.3	85.9
1.30	83.7	86.4
1.37	83.7	87.0
1.43	83.2	86.4
1.50	83.2	86.4
1.57	82.1	85.4
1.64	81.6	85.4

The foregoing data in which columns G

and H list the % desulfurization show that the rate of deactivation of Catalyst H is considerably lower than that of Catalyst G.

EXAMPLE X (for Comparison)

In this example 300 grams of the commercially obtainable cobalt molybdenum catalyst pellets used in Example I are impregnated with 200 ml. of a solution of chloroplatinic acid containing 0.9g platinum. After standing for one hour at room temperature the catalyst is dried overnight at 250°F. Calcination is carried out in a flow of air at 900°F. The catalyst contains 0.3 wt. % platinum.

EXAMPLE XI

180 g of commercial catalyst pellets used in Example IX are impregnated with a solution of 0.45 g of rhodium trichloride dissolved in 125 cc of H_2O. After standing at room temperature with occasional mixing for one hour, the impregnated catalyst is dried at 250°F. for 64 hours. The impregnated catalyst is calcined at 900°F. for 2 hours in a flow of air. It contains 0.1 wt. % rhodium.

The catalysts prepared in Examples X and XI above are evaluated against the unimpregnated catalyst by desulfurization of West Texas-New Mexico Sour vacuum gas oil containing 1.9 wt. % sulfur at a temperature of 800°F., a pressure of 800 psig, and a space velocity of 4 v/v/hr. in the presence of hydrogen introduced at a rate of 500 scf fresh hydrogen and 1500 scf recycle hydrogen per barrel of feed.

The results are tabulated below, the length of the on stream period being reported in terms of barrels of charge per pound of catalyst, with the column headed Base Run listing the percent desulfurization of the unimpregnated catalyst and the columns headed X and XI listing the percent desulfurization of the respective catalysts

TABLE 10

Throughput (bbl./lb.)	*Base Run*	*X*	*XI*
0.5	90.8	92.6	—
0.6	90.7	92.4	—
0.7	90.6	92.3	—
0.8	90.5	92.1	—
0.9	90.4	92.0	92.4
1.0	90.3	91.9	92.4
1.1	90.2	91.7	92.3
1.2	90.1	91.6	92.2
1.3	90.0	91.5	92.2
1.4	89.9	91.4	92.1
1.5	89.8	91.3	92.1
1.6	89.7	91.1	92.1
1.7	89.6	91.0	92.0
1.8	89.6	90.9	92.0
1.9	89.5	90.8	91.9
2.0	89.4	90.7	91.9
2.1	89.3	90.7	91.9
2.2	89.2	90.6	91.8
2.3	89.2	90.5	91.8
2.4	89.1	90.4	91.7
2.5	89.0	90.3	91.7
2.6	89.0	90.3	91.7

EXAMPLE XII

In this example, 300 grams of the same commercially available desulfurization catalyst used in Example IX is impregnated with an aqueous solution containing 0.6 g of $IrCl_4.4H_2O$ in 189 cc. of water. After standing at room temperature with occasional mixing for several hours, the impregnated catalyst is dried at 250°F. for 64 hours and then calcined at 1000°F. for two hours. The resulting catalyst contains 0.1 wt. % iridium. This catalyst is evaluated against the unimpregnated catalyst by making comparative runs using as charge stock an Arabian vacuum gas oil containing 2.37 wt. % sulfur in which the charge is passed through a bed of catalyst pellets. The reaction conditions are less severe in this example than in Example X and XI in that as in Example IX the pressure here is only 400 psig. The other conditions are a temperature of 800°F., a space velocity of 4 v/v/hr. with hydrogen introduced at a rate of 2000 scfb of which 500 scf is fresh hydrogen and 1500 scf is recycled hydrogen. The results are tabulated below, throughput being measured in terms of barrels of charge per pound of catalyst, and the column headed "Base Run" showing the % desulfurization using the unimpregnated catalyst and that headed "XII" showing the % desulfurization using the catalyst containing 0.1 wt. % iridium. It will be noted again that the deactivation rate of catalyst XII is lower than that of the unimpregnated catalyst.

For a true comparison, in each of these examples the unimpregnated catalyst is subjected to the same calcination treatment as the impregnated catalyst with which it is compared.

TABLE 11

Throughput	*Base Run*	*XII*
0.26	87.1	87.7
0.33	86.7	87.3
0.39	85.4	86.9
0.46	84.9	86.0
0.53	84.1	84.8
0.59	84.1	84.3
0.66	83,2	83.1
0.72	83.2	83.5
0.79	83.4	83.5
0.86	81.5	82.7
0.92	81.9	83.5
0.99	80.6	83.1
1.06	80.6	82.7
1.12	81.1	82.7
1.19	81.1	81.8
1.26	80.6	81.4
1.32	80.6	81.8
1.39	79.8	81.8

These examples show that under the conditions emyloyed, that is, at high temperatures and high space velocities, the catalysts impregnated with noble metals do not have significantly higher initial activity than the unimpreganted catalysts but their deactivation rate is noticeably lower.

WHAT WE CLAIM IS:

1. A method for hydrodesulfurizing a heavy petroleum distillate oil having an initial boiling point of at least 500°F, which comprises contacting said oil with hydrogen in the presence of a fixed bed of a particulate catalyst comprising an iron group metal, or compound thereof, and a Group VI A metal, or compound thereof, supported on a base comprising a refractory inorganic oxide at a temperature of from 750 to 850°F. and a space velocity of from 3 to 10 v/v/hr.

2. A process as claimed in Claim 1 wherein the pressure is at least 500 psig.

3. A process as claimed in Claim 2 wherein the pressure is from 500 to 3000 psig.

4. A process as claimed in any preceding claim wherein the iron group metal is nickel or cobalt.

5. A process as claimed in any preceding claim wherein the catalyst contains 1 to 10% by weight of iron group metal.

6. A process as claimed in any preceding claim wherein the Group VI A metal is molybdenum or tungsten.

7. A process as claimed in any preceding claim wherein the catalyst contains 5 to 30% by weight of the Group VI A metal.

8. A process as claimed in any preceding claim wherein the refractory inorganic oxide is silica, alumina, magnesia, zirconia or a mixture thereof.

9. A process as claimed in any preceding claim wherein the space velocity is between 4 and 8 v/v/hr.

10. A process as claimed in any of claims 1 and 4 to 9 wherein the catalyst comprises from 0.1 to 5% by weight, based on the catalyst composite, of a Group VII metal or compound thereof.

11. A process as claimed in Claim 10 wherein the Group VII metal is rhenium or manganese.

12. A process as claimed in claim 10 or 11 wherein the catalyst contains between 0.2 and 2.0% by weight of the Group VII metal.

13. A process as claimed in any of claims 1 to 9 wherein the catalyst comprises from 0.1 to 5% by weight of a noble metal, based on the weight of the catalyst composite.

14. A process as claimed in Claim 13 wherein the noble metal is platinum, rhodium or iridium.

15. A process as claimed in claims 13 or 14 wherein the catalyst contains from 0.2 to 2.0% by weight of the noble metal.

16. A process as claimed in any of claims 10 to 15 wherein the pressure is between 300 and 500 psig.

17. A process as claimed in any preceding claim wherein the support contains alumina and not more than 5 wt. % silica, based on the catalyst composite.

18. A process as claimed in any preceding claim wherein the temperature is between 800 and 850°F.

19. A method as claimed in claim 1 substantially as hereinbefore described with reference to any of Examples I to IV.

20. A method as claimed in claim 1 substantially as hereinbefore described with reference to any of Examples V to VIII.

21. A method as claimed in claim 1 substantially as hereinbefore described with reference to any of Examples IX, and XI to XII.

22. Petroleum oil when hydrodesulfurized by a method according to any preceding claim.

MICHAEL BURNSIDE & PARTNERS

Chartered Patent Agents
Hancock House
87 Vincent Square
London SW1P 2PH
Agents for the Applicants

Printed for Her Majesty's Stationery Office by The Tweeddale Press Ltd., Berwick-upon-Tweed, 1976. Published at the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.